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Research Article

Oligomerization of C_2-C_4 Hydrocarbons in the Presence of Ruthenium-Nickel Supported Catalysts

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Abstract

The oligomerization of C_2-C_4 light hydrocarbon gasses in the presence of ruthenium and nickel supported catalysts is investigated. Determined selectivity of the catalysts by isooctane. Catalytic properties of the catalysts depend on the supported metals on the carrier. The nature of carrier also affects on reaction selectivity. The ruthenium-nickel supported bimetallic pillared montmorillonite is showed good selectivity to isooctane and value is about 60.8% at conversion 87.0%.

Keywords: oligomerization; montmorrillonite; isooctane; ruthenium; nickel

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1. Introduction

One of the most important problems of oil refining and petrochemical synthesis concerns the development of effective technologies to obtain high-octane components used as motor fuels. In this regard, the production of motor fuels through oligomerization of light hydrocarbons is interesting because the obtained products do not contain sulfur-, nitrogen- and oxygen compounds or toxic organic compounds which have negative impact on the environment and human health [1].

Light olefins oligomerization reaction can be catalyzed by homogeneous or heterogeneous systems. However, the use of heterogeneous catalytic systems enables an easier product/catalyst separation corresponding to a more environmentally friendly process if compared with homogeneous catalytic systems. Currently, synthetic aluminosilicate is often used as a support of metallic-based catalysts in solid-gas oligomerization process [2-5]. During the oligomerization reaction, long-chain of hydrocarbons are formed which can block the pores of the support leading to a fast deactivation of the catalysts [6-8]. Whereas larger pore size zeolites also quickly deactivated [9,10], mesoporous zeolites are considered-adapted support of catalysts to perform the oligomerization of C_2-C_4 hydrocarbons to produce gasoline and diesel range products. Bentonite, a natural clay, is a low-cost material which has an excel-

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lent cation exchange capacity [11-13]. Bentonite are currently used as precursor of "Pillar structure" materials which are even more attractive as support of catalyst as they present an expanded cell structure, where the main material is montmorillonite. In Kazakhstan there are large deposits of natural minerals which are available to be used as adsorbents and catalyst support. Aluminum polyoxocations are the most commonly used as a pillaring agent. In order to improve the catalytic activity of the clays Bradley *et al*. synthesized Ga polyoxocation and use it instead of Al because of the same electronic configuration of Ga and Al, their chemical properties similar to etch other. Also, Ga-being more atomic number (31) than Al. As a result, stability of the $GaAl_{12}$ Keggyn structure was increased [10].

Catalysts having high hydrothermal and mechanical robustness are obtained combining two metals, one of them having a high melting point and being a nobel metal. Bernard Coq *et al.* are the authors of a brief review of the bimetallic catalysts performance [14]. The oligomerization of ethylene most commonly employs Ni-based bifuntional catalysts [15,16]. Besides Ni and Ru individual has been extensively studied at hydroconversion reactions such as hydrogenation of aromatic compounds [17,18]. In addition, the type of joint NiRu- supported bimetallic catalysts have also been applied in CO_2 reforming of methane and methane steam reforming reactions [19,20].

This study describes the synthesis and the characterization of Ga-pillared montmorillonite (MMG) used as support of Ni-Ru catalyst. The catalytic behavior of the resulting catalysts Ru-Ni-MMG (montmorillonite modified by Gallium compound-MMG) is evaluated in the oligomerization of C_2-C_4 hydrocarbons to produce motor fuels. The catalysts were characterized by N_2 adsorption, SEM and TEM analysis.

2. Materials and Methods

2.1 Support preparation

Commercial γ–Al_2O_3 (Alfa Aesar, 99.97%) and natural montmorillonit (MM) clay (Republic of Kazakhstan) are used without further treatment as starting materials. Gallium nitrate - $Ga(NO_3)_3$ (Topan TOO, Uralsk, Kazakhstan, 99.999%) is used as a structuring agent to sythesize a pillared montmorillonit clay based on procedures described in the literature [21,22]. The parent clay is first saturated with sodium ions through exchange with 1 M NaCl solution for 8h, then washed with deionized water in order to remove residues of NaCl. After that, a 0.1 M NaOH solution is added to an aqueous solution of $Ga(NO_3)_3$ under vigorous stirring at room temperature. To this mixture is added the clay forming a suspension stirred during 4 h. After filtration, the solid is dried in air at ambient temperature. Finally, the modified clay (MMG) is calcined at 450 °C (heating rate of 2 °C/min) during 8h in air. Thus, the MMG, a pillared clay, is the used as support of Ru and/or Ni species.

For improving the swelling properties of the clay used 1 M NaCl solution. As support used Ruthenium(III) chloride-$RuCl_3 \cdot 3H_2O$ and hexahydrate of nickel(II) nitrate- $Ni(NO_3)_2 \cdot 6H_2O$.

2.2. Catalyst preparation

Ruthenium and nickel based catalysts were prepared employing $RuCl_3 \cdot 3H_2O$ (99.99 %, Alfa-Aesar) and hexahydrate of nickel(II) nitrate (99.99%, Sigma-Aldrich) salts as precursor. The 1.0% Ru/γ-Al_2O_3 catalysts was prepared through classic impregnation using 20 mL of an aqueous solution (distilled water) of the ruthenium salt in which a chosen mass of the supports is added. This suspension is then stirred for 3 hours, dried at 120 °C for 6 hours and, finally the resulting solid is calcined in air at 500 °C for 4 hours. Mono and bimetallic catalysts (MMG as a support) containing Ru and Ni were prepared by incipient wetness co-impregnation of the supports with aqueous solutions of the precursors containing the desired amount of the respective salts. The impregnated solids are then dried at 80 °C for 8 h and calcined at 450 °C during 6 h in the air at heating rate of 2 °C/min.

2.3 Characterization techniques

Textural properties of the samples are obtained from nitrogen adsorption-desorption isotherm experiments, measured at 77K using an ASAP 200 Mirometric instrument. The specific surface area (SSA) values and the mean pore size diameters are determined applying Brunauer Emmett and Teller (BET) and Barrett-Joyner-Halenda (BJH) - methods, respectively. Scanning electron microscopy (SEM) - images of the sample previously gold-coated are performed using a Jeol JSM 5800 microscope (20 kV) equipped with a secondary electron images detector. To characterize the solid samples by transmission electron microscopy (TEM) carried out in a Philips CM20 (200 kV) microscope, powder solid is added to isopropanol. The resulting suspension is for 1 min, one drop is placed on a carbon-coated copper grid which is dried to eliminate isopropanol.

2.4 Catalytic tests

Oligomerization of light hydrocarbons is carried out in a continuous flow fixed-bed reactor in the reaction temperature range 110-170 °C and with a light olefin pressure of 2.0 MPa. Prior to experiment the catalyst (1 g) is pretreated in situ in a stream of hydrogen (50 cm^3/min) at 300 °C under atmospheric pressure during 2 h. Then the reactor is cooled down until the reaction temperature under a flow of argon (Ar, 50 cm^3/min). After that the C_2-C_4 gas mixture is introduced to the reactor. Reaction products are analyzed employing a DANI Master GC Fast Gas Chromatograph.

3. Results and Discussion

Table 1 reports physicochemical properties data of the parent supports and the metal supported catalysts. SSA value of MMG is larger than those of MM (250 and 60 m^2/g) confirming the effective modification of the clay after being modified with Ga. SSA values registered for γ–Al_2O_3 and Ru/γ-Al_2O_3 are almost similar, changed from 190 to 180 m^2/g. Comparing MMG to Ru/MMG and RuNi/MMG, the SSA changed from 250 to 240 and 235 m^2/g, respectively. These slight reductions of the SSA values are a consequence of the presence of the metal oxides on the surface of the catalyst.

The modification of the MM clay leading to its pillarization is accompanied by an increase of the mean pore size value (from 1.1 nm to 4.4 nm). This data confirm that the MM clay has been successful pillared by the addition of gallium, modification which is important for increasing the exchange capacity [23]. In the case of γ-Al_2O_3, the presence of Ru leads to the decrease of the mean pore size value (4.7 to 4.0 nm). At the contrary, in the case of MMG, the presence of Ru and NiRu increases slightly the mean pore size values 4.4 to 4.6 and to 4.5 respectively. As these values are deduced from N_2 adsorption/desorption experiments these results indicate that the MMG pillared structure allows the introduction of the metallic ions between the layers freely differently to what occurs with γ-Al_2O_3.

XRD patterns of the montmorillonite and Ru -Ni supported montmorillonite (modified by Gallium compound) presented in Figure 1. It can be seen after modification and addition of metal do not influenced the clays crystalline structure. The characteristic peaks for Ni and Ru identified - 38˚, 70˚ and 28˚, 57˚, respectively. It is obvious that the Ru and Ni species well dispersion in the clay layer. This may indicate that slightly decrease BET surface area observed from for this samples, due to NiO and RuO_2 nanoparticles have to be located internal surface of the clay, as discussed about (Table 1).

The morphology of the pillared clays MMG compared to the parent clay (MM) investigated by SEM analysis as shown in Figure 2. Even the three micrographs have different resolutions. It can be observed that MM clay has a layered structure (Figure 2 A) and at the same magnitude that MMG shows that an important structure modification occurred due to the pillarization procedure (Figure 2 B and C). Figure 1A evidences that the MM structure is formed by parallel layers similar to the mica structure.

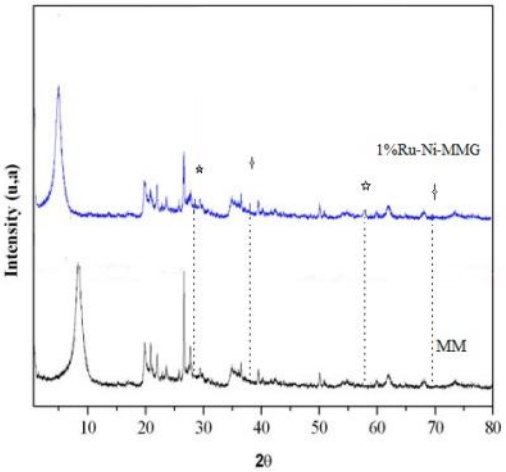

Figure 1. XRD patterns of parent (MM) and metal supported (1%Ru-Ni-MMG) carrier

Table 1. Physicochemical properties of the parent carrier and metal supported catalysts

Samples	Ru content, (wt %)	Ni content, (wt %)	SSA[b] (BET), m^2/g	Mean pore diameter, nm
Γ-Al_2O_3	-	-	190	4.7
MM	-	-	60	1.1
MMG[a]*	-	-	250	4.4
1.0 %Ru/γ-Al_2O_3	1.0	-	180	4.0
1.0 %Ru/MMG*	1.0	-	240	4.6
1.0 %RuNi(Ru:Ni=1:1)/MMGa*	0.5	0.5	235	4.5

[a]*Mont morillonite modified by Gallium compound addition. [b]SSA: Specific Surface Area

This structure is consistent the montmorillonite belong to the 2:1 phyllosilicate family. Its inner layers are consisting of an octahedral sheet of alumina sandwiched with two tetrahedral sheets of silica. Such a layer structure is stacked by weak dipolar or van der Waals forces. This structure leads to the exchangeable ions layout into the internal surface [24]. Otherwise Figure 2 C shows that the presence of Ga leads to a new texture confirm that the layered structure characterizes the MM materials is completely modified after the introduction of Ga.

TEM images of MMG and Ru-Ni-MMG are shown in Figure 3. Comparing to original support (MM) with the modified one (MMG) presented respectively Figures 2 and 3, the distance between the layers increases from 1.0 nm to 3.5 nm. An ordered crystal formed by long parallel plans is detected for the MMG materials (Figure 3A). Similar results have been described by Wang *at al.* concerning a TiO_2-Montmorillonite pillared clay [25]. The presence of larger spaces between the layers is suitable for the transit of large molecules into the pores of the clay. Figure 3B shows the presence of well distributed small particles (in the range 3.4 to 5.2 nm) of metallic oxide indicating well dispersed Ru and Ni particles into the clay support.

The conversion and selectivity values calculated for the conversion of C_2-C_4 hydrocarbons at various reaction temperature are given in Table 2. It is shown that yields of C_8, C_{10} olefin fractions increased with reaction temperature and it was well selective by isooctane, 60.8%. Share of these oligomers from the obtained products has maximum at 150 ^{0}C. This affects the same as NiO-W_2O_3/Al_2O_3 catalyst [26]. At that temperature gas conversion reached 87%. On the con-

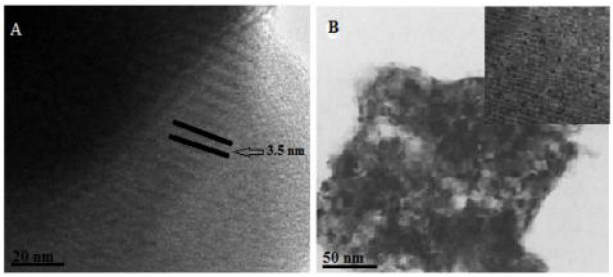

Figure 3. TEM images of MMG (A) and with Ru-Ni-MMG (B)

Table 2. Oligomerization of C_2-C_4 hydrocarbons at presence of metal supported heterogeneous catalysts (Reaction conditions: P = 2.0 MPa; reaction time = 30 min.)

Catalysts	Temperature, ^{0}C	Oligomer distribution (wt%)				Selectivity by isooctane, %	Conversion, %
		$C_6^=$	$C_8^=$	$C_{10}^=$	$C_{12+}^=$		
1.0 %Ru/γ–Al_2O_3	110	-	19.5	9.8	12.5	38.6	55.3
	130	2.3	21.4	11.7	11.1	43.0	59.0
	150	3.1	28.0	13.5	6.9	46.1	61.2
	170	2.6	32.1	16.1	5.1	48.4	64.5
1.0 %Ru/MMG*	110	-	24.5	14.0	14.9	43.8	59.0
	130	3.0	27.1	16.6	10.6	48.1	63.7
	150	4.2	33.8	17.9	8.0	55.7	69.1
	170	3.4	30.5	19.1	5.2	51.9	64.2
1.0%RuNi(Ru:Ni=1:1)/MMG*	110	1.0	29.6	15.7	12.4	45.5	75.0
	130	3.9	33.5	17.0	11.7	49.9	79.2
	150	4.5	41.2	20.0	10.8	60.8	87,0
	170	4.0	34.3	22.1	9.1	51.0	81.4

*Montmorillonite modified by compound Gallium

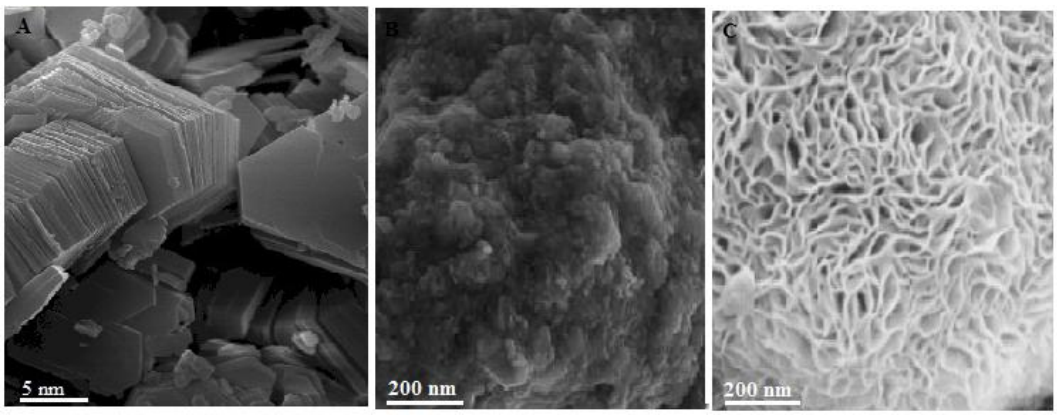

Figure 2. SEM images of parent MM (A, B) and MMG* (C)

trary the yield of C_6, C_{12+} fractions decreased and had a very low yield occurred on C_6 fraction. It can be explained as follows: at high temperature occurs splitting of the molecules of hydrocarbons, i.e. decomposition of C_{12+} olefins forming C_8 and C_4 or C_{10} and C_2 fractions. This leads to increasing the selectivity of isooctane yield. The temperature dependence of the division of oligomer had been studied by Alcantara *et al*. [27] since oligomer splitting moves toward more important side at temperature above 100-110 ^{0}C. During the C_2-C_4 oligomerization reaction to form di-, tri- or high molecular weight hydrocarbons depends on the metal content and their dispersion on surface of the carrier. Comparing to the both mono and bimetallic oligomerization catalysts, the Ru- based catalysts less active than Ru-Ni system. This behavior is in agreement with that the presence of Ni strongly improved catalytic activity of the Ru-based catalyst while Ru play as a role of stabilization and prevention rapid deactivation of the nickel due to the coke formation. It was studied by several authors [28-30]. This suggests that the carbon species formed on the surface of the Ru-Ni samples a high reactivity, thus limiting the deactivation of the catalyst.

The stability of the Ru/MMG and RuNi/MMG catalysts for oligomerization of C_2-C_4 hydrocarbons were also evaluated. The conversion of C_2-C_4 hydrocarbons as function of the time were shown in Figure 4. Taking into account the stability of the catalysts each 1 h on stream, the Ru-Ni/MMG catalyst showed relatively stable for 7 h, then the conversion of gas started to decrease until 68 and stabilized to 65%. For the Ru/MMG catalyst, conversion of gas slightly declined to 43%, then after 6 h stabilized to 40%. These results show that the bimetallic catalyst more active and stable than monometallic one, which might result from the well dispersed nickel is encapsulated by ruthenium to form larger clusters that limits nickel nanoparticle deactivation during the reaction [31,32]. After 7 h the deactivation accruing on bimetallic catalyst, it is because of some nickel nanoparticle outside of clusters that coated with coke which collected over longer reaction time immediately reduced catalyst activity. As well as due to the agglomeration of Ru nanoparticles on the MMG surface the monometallic catalyst gradually deactivated.

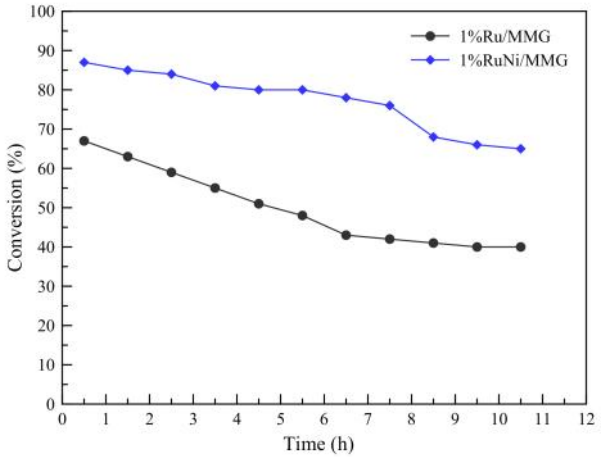

Figure 4. The conversion of C_2-C_4 hydrocarbons at different catalyst loadings with time on stream (150 ^{0}C, P = 2.0 MPa)

4. Conclusions

On the base of catalytic activity and characterization date reported in this paper to conclude that the diversity of the nature carrier and planted metal has played key role on the light hydrocarbon oligomerization reaction. The catalysts supported on pillar structural clay carrier showed best catalytic activity for C_2-C_4 oligomerization reaction under mild condition. BET, SEM and TEM characterization results indicated that the pillared montmorillonit by gallium has ordered mesoporous structure. It allows to larger molecules that formed by during the reaction can enter into the pore easily to avoid pore blocking process. Furthermore, the catalytic behavior of the Ru-Ni bimetallic catalysts strongly depends on the second metal used. The best result in terms of activity and stability are obtained on the 1.0% RuNi/(Ru:Ni=1:1)/MMG catalysts at P = 2.0 MPa, t = 150 ^{o}C, selectivity to iso-octane yield 60.8%, when the conversion of gas reached 87.0%.

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